ORGANIC GEOCHEMISTRY OF THE NEW ALBANY SHALE IN ILLINOIS

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ABSTRACT

The Mississippian-Devonian New Albany Shale Group was sampled over a 35,000 square-mile area in the southern two-thirds of Illinois. The samples were subjected to an organic geochemical investigation to determine their qualities as petroleum source rocks. In the very dark-colored bottom 50 feet of this shale, organic carbon content averages slightly over 4 percent by weight. Benzene soluble compounds (both hydrocarbons and nonhydrocarbons) make up as much as 0.2 percent of the weight of the rock.

The total volume of benzene extractable compounds in the bottom 50 feet of shale is 50×10^9 barrels (bbls). This is 100 times more than the total volume of oil found in the underlying Devonian-Silurian reservoirs.

The organic geochemical data suggest the New Albany Shale as a likely source of most of the Devonian-Silurian oil in Illinois.

INTRODUCTION

The Oil and Gas and Organic Geochemistry Sections of the Illinois State Geological Survey are currently conducting a geochemical investigation of the nonreservoir rocks in Illinois. These rocks are shales and dense carbonates that are not generally considered as potential producers of oil and gas. They are important in the accumulation of oil and gas where they have served as the source rocks that generated the hydrocarbons.

The purpose of the organic geochemical study is to determine the relative importance of the rocks in Illinois with respect to their qualities as petroleum source rocks. No generally accepted criteria have been established for recognizing a petroleum source rock, regardless of the amount of geochemical data that may be available. Nearly all shales and carbonates contain indigenous organic compounds including hydrocarbons (Hunt and Jamieson, 1958), and thus the mere presence of hydrocarbons does not distinguish source rocks.

Various organic geochemical studies made in other sedimentary basins have resulted in the proposal of certain criteria for distinguishing source rocks from nonsource rocks. These criteria generally are based on the carbon content of the rocks and the forms in which it occurs. Car-

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bon may be found in the various carbonate compounds or as a part of organic compounds, either hydrocarbons or nonhydrocarbons. References to some of these studies are made in this report where it is felt that the conclusions are pertinent to this study.

In the initial stages of this study it was necessary to choose a rock unit that was thought to be a likely petroleum source rock. The New Albany Shale Group (Mississippian-Devonian) was chosen because of the geologic evidence suggesting that it served as a source of much of the oil found in the underlying Hunton Limestone Megagroup (Devonian-Silurian).

Swann and Bell (1958, p. 455) stated that all known Devonian and Silurian oil pools in Illinois are found within 100 feet of the base of the New Albany. This, however, is no longer entirely true, as some reservoirs in the Dutch Creek Sandstone Member at the base of the Grand Tower Limestone (Devonian) later were found to produce oil in the deep part of the Fairfield Basin more than 200 feet below the base of the New Albany. The vast majority of the Devonian-Silurian oil, nevertheless, both in terms of volume and number of pools, comes from the top 100 feet of the Hunton Limestone Megagroup. This suggests that the oil was generated either in the New Albany or in the underlying Devonian and Silurian carbonates. The latter possibility appears remote because of the long period of time during which these carbonates were exposed to erosion, prior to being buried by the New Albany Shale. Any oil generated in the upper part of the Hunton surely would have been lost before the New Albany Shale could have sealed it in the reservoirs.

Previous studies of oil shales in Illinois have shown that the New Albany will yield oil when heated to destructive distillation temperatures (Lamar, Armon, and Simon, 1956). Lineback (1968, p. 1292) found the organic carbon content of some New Albany samples in Indiana to be as high as 20 percent by weight. He suggests that the major portion of this organic material was deposited with the New Albany Shale as a continual rain from mats of floating algae (Lineback, 1968, p. 1301).

The purpose of this paper is to present some geochemical data in support of the geological evidence suggesting that the New Albany Shale is a likely petroleum source rock.

PETROLEUM GENERATION AND MIGRATION FROM SOURCE ROCKS

The generation of oil in a source rock probably begins quite soon after deposition of the sediments and continues for a long time. Philippi (1965) presents evidence that indicates small amounts of hydrocarbons in very young sediments, perhaps even at the time of deposition. He shows that the generation of oil is a thermal, nonbiological process acting on the organic material in the sediments.

Kidwell and Hunt (1958), working with clays and sands of the Orinoco River delta in Venezuela, found evidence of generation and migration of hydrocarbons in sediments less than 10,000 years old. Their studies support what is probably one of the most plausible theories of oil migration. They postulate that minute quantities of oil are carried by the interstitial water forced out of a clay as it is compacted under the weight of continuing sedimentation. The oil conceivably could be carried in three ways: (1) in solution, (2) as a colloidal dispersion, or (3) as droplets of oil. Their conclusion, based on the very low concentrations of hydrocarbons in water produced from sands (less than 16 ppm), is that the oil must be in solution or in the form of a very dilute colloidal dispersion (Kidwell and Hunt, 1958, p. 814).

Assuming that this is the way the oil migrated from the New Albany Shale, then the oil in the upper part of the Hunton Limestone Megagroup is likely to be the concentrated and trapped portion of the oil filtered from the water that was squeezed out of the bottom of the overlying shale.

Before this explanation can be accepted, the New Albany must be found to contain hydrocarbons similar to those found in crude oil. The analytical methods for determining hydrocarbon content involve organic carbon analysis, benzene extraction, and chromatographic analyses of the extract. These techniques will be discussed in more detail in a later section of this report.

ORGANIC GEOCHEMICAL ANALYSIS

Sampling Techniques

New Albany Shale samples are available in three different forms. Diamond cores of a limited number of holes provide a relatively large sample making a variety of analyses possible. Outcrop samples around the Illinois Basin margin provide samples of equally adequate volume, but they are weathered and available in only a few localities. The only abundant samples offering statewide coverage are drill cuttings. Unfortunately, cuttings necessitate careful selection of the desired New Albany chips from cavings, and only

provide enough material for an analysis of the carbon content.

Sample Preparation

Before organic material can be extracted from a core sample, the rock must be reduced to a fine powder. This was done in a three-step process. First, a jaw crusher reduced the core to fragments about $\frac{1}{4}$- to $\frac{1}{2}$-inch in their longest dimension. Second, these fragments were fed through a roller mill to further reduce the particle size. Finally, a Raymond pulverizer produced a fine rock powder that would pass through a 100-mesh sieve.

The outcrop samples were taken from a zone 6 inches to 1 foot below the surface. At this shallow depth, weathering had reduced the shale to fairly small fragments, and thus the samples could be processed without the use of the jaw crusher. These samples were handled in much the same manner as were the cores.

Drill cuttings presented more problems than other types of samples because of contamination by cavings. The various sample sacks representing the interval to be sampled were examined separately. A quantity of chips believed to be representative of the depth marked on the sack was separated from the remainder. Approximately equal quantities were selected from each bag so that when they were combined to form one sample, it was representative of the entire sampled interval. The cuttings were then ground to a minus 100-mesh particle size before analysis.

Analytical Procedure

Organic carbon content

The total carbon and carbonate carbon content of each shale sample was determined analytically. The organic carbon content was then calculated as the difference between the two above values.

Total carbon was determined by an adaptation of the British Standard, "Methods for the Analysis and Testing of Coal and Coke" (British Standards Inst., 1958). This method is similar to the American Society for Testing and Materials method (ASTM designation: D271-68) except that a tube furnace temperature of 1350° C is used.

Carbonate carbon was determined by an adaptation of the ASTM standard method of test for carbon dioxide in coal (ASTM designation: 1756-62). This procedure is equivalent to the one described in the British Standard Methods cited above. All total carbon and carbonate carbon analyses were performed by the Analytical Chemistry Section of the Illinois State Geological Survey.

Benzene extractable organic matter

The benzene extractable organic matter generally amounted to only a small percentage of the total organic matter contained in the sample, as indicated by the organic carbon value obtained.

A 250 g pulverized rock sample was extracted for 40 hours with 1250 ml of redistilled benzene in a modified Soxhlet extraction apparatus (Kontes Glass Co.; fig. 1). This apparatus employs a 60 x 150 mm thimble capable of holding a 250 to 400 g sample of pulverized rock.

In order to minimize channeling, a 10 x 150 mm thimble fitted with a small glass funnel was positioned in the center of the large extraction thimble. The recondensed solvent in this way is made to flow radially from the center of the sample to the outside.

The thimble well of this extractor is jacketed in such a manner that the solvent in contact with the rock sample is at the solvent boiling point. After the 40-hour extraction period, the benzene solution is concentrated to 4 or 5 ml by distillation. The concentrate is transferred to a weighing vial through a small sintered glass filter, and the last trace of benzene is removed under a stream of nitrogen. The weight of the benzene extractable organic matter is then determined.

Activated alumina column chromatography

All solvents used in the column separation were of reagent grade and were redistilled. Chromatographic alumina (Alcoa grade F-20) was activated at 225° C for 48 hours before introduction into the column. The glass columns were 12 mm outside diameter (O.D.) by 100 cm in length and were fitted with Teflon stopcocks (fig. 2).

A small wad of glass wool was placed in the bottom of the column and overlain with a $\frac{1}{4}$-inch layer of organic-free silica sand. Activated alumina was added dry to a depth of 24 inches and packed with the aid of a Vibro-tool. The activated alumina was overlain with another $\frac{1}{4}$-inch layer of sand, and 4 or 5 ml of n-heptane was added slowly to the top of the column and allowed to run down to within 1/8-inch of the top of the sand. The stopcock was closed, and the sample (usually 100 to 500 mg of the benzene extract) dissolved in n-heptane was introduced onto the column.

The column was eluted in order with 30 ml of n-heptane, 30 ml of benzene, and 30 ml of a 1:1
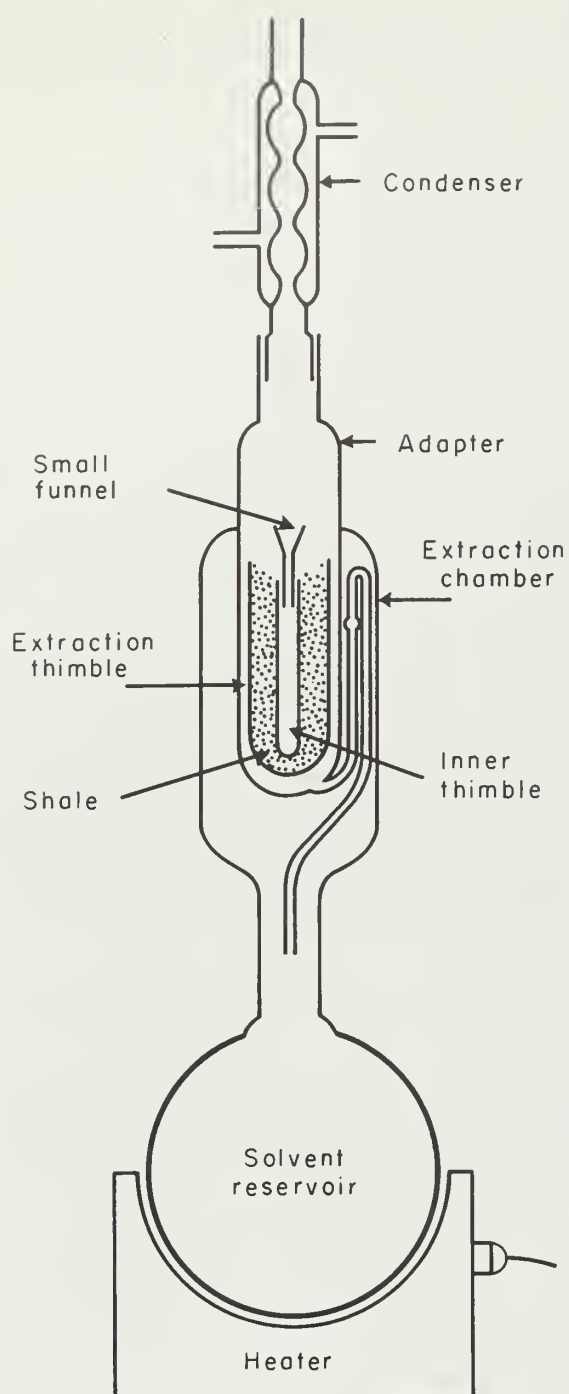
Fig. 1 - Soxhlet extractor used in extracting or-
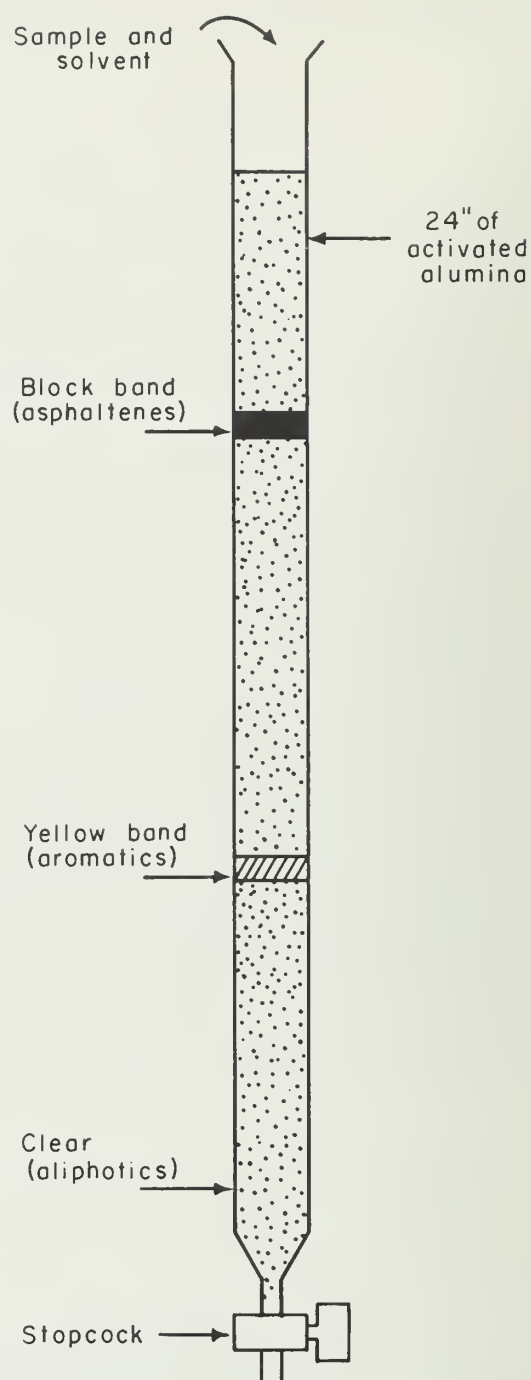ganic matter from shale samples.

Fig. 2 - Chromatographic column used to sepa-
rate benzene extractable organic matter into
aliphatic, aromatic, and asphaltene frac-
tions.

(volume to volume) mixture of methanol and benzene to give three fractions, which were collected in three separate 50 ml Erlenmeyer flasks.

The first fraction contains the aliphatic (straight- and branched-chain) hydrocarbons; the second fraction contains the aromatic (ring-containing) hydrocarbons; and the third fraction contains the nonhydrocarbons (asphaltenes).

The fractions were concentrated down to 4 or 5 ml by evaporation on a steam bath and then carefully transferred to small weighing vials. The last traces of solvent were removed on a steam bath under a stream of purified nitrogen, and the weight of the fraction was determined. The benzene extraction and column chromatography were performed by the Geological Survey's Organic Geochemistry Section.

Results of Analyses

The relationships of the various organic constituents to each other can best be illustrated by the analytical results obtained from a core cut through the entire New Albany section. The core was taken during the drilling of the Miller #1 G. W. Sample hole in Sec. 11, T. 15 N., R. 3 W., Sangamon County, Illinois. Samples were selected from the core more or less on the basis of color with a representative sample being taken from each interval showing a distinctive color. Some intervals of 20 feet or more show no color variation, and thus these long intervals were sampled every 10 to 20 feet.

Figure 3 illustrates the organic content of the shale samples by means of line graphs. The left-hand graph shows the organic carbon content in percent by weight; the right-hand graph shows the percent by weight of benzene soluble organic matter. The two curves are quite similar and show a marked increase in organic matter toward the lower part of the shale. This trend is reversed near the base of the shale, however, where the content of organic carbon and benzene extractable matter decreases rather abruptly.

The close relationship between organic carbon content and benzene extractable organic matter is very apparent in figure 3. To further emphasize this relationship, the percentage of organic carbon versus the percentage of extracted matter was plotted in figure 4, and a regression line was fitted by the least-squares method (Brunk, 1960, p. 199-200). The correlation coefficient of these data is 0.978. This type of correlation has been used as an indication of a genetic relationship be-
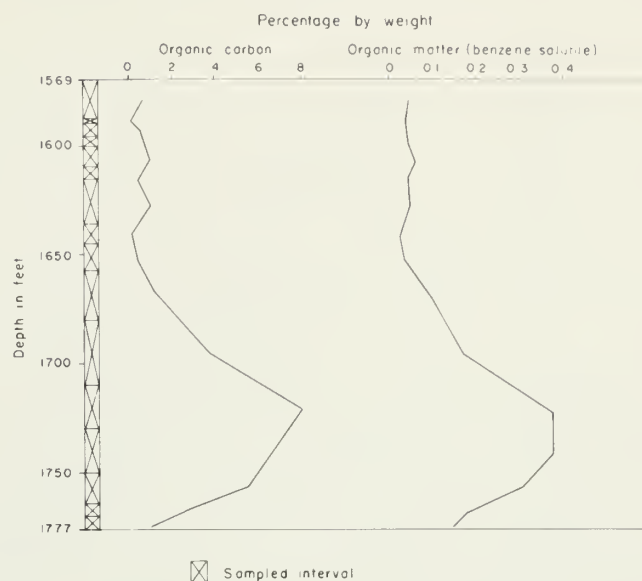

Fig. 3 - Results of geochemical analysis of New Albany Shale from the Miller #1 G. W. Sample, Sec. 11, T. 15 N., R. 3 W., Sangamon County, Ill.

tween extracted oil and indigenous organic matter. If the two are genetically related, then the oil is indigenous also and the rock is an oil-source formation (Philippi, 1956, p. 29-30). This close relationship may also suggest that the organic carbon content indicates the amount of organic material available for transport out of the shale in solution or as a colloidal dispersion during compaction.

A regional study of organic carbon content of the New Albany Shale Group was made to determine if the location of known oil pools in the Hunton Limestone Megagroup has any relation to the amount of organic carbon in the overlying shale. In order to avoid correlation problems encountered by trying to sample only specific formations, an arbitrary unit was chosen consisting of the bottom 50 feet of the New Albany Shale. If the assumption that the oil moved out of the bottom of the shale into the underlying reservoirs is a valid one, the bottom 50 feet of shale should have comprised a large part of the total source rock.

Figure 5 is a contour map showing the organic carbon content of the bottom 50 feet of the New Albany Shale and the location of the known oil and gas pools in the Hunton Megagroup. The
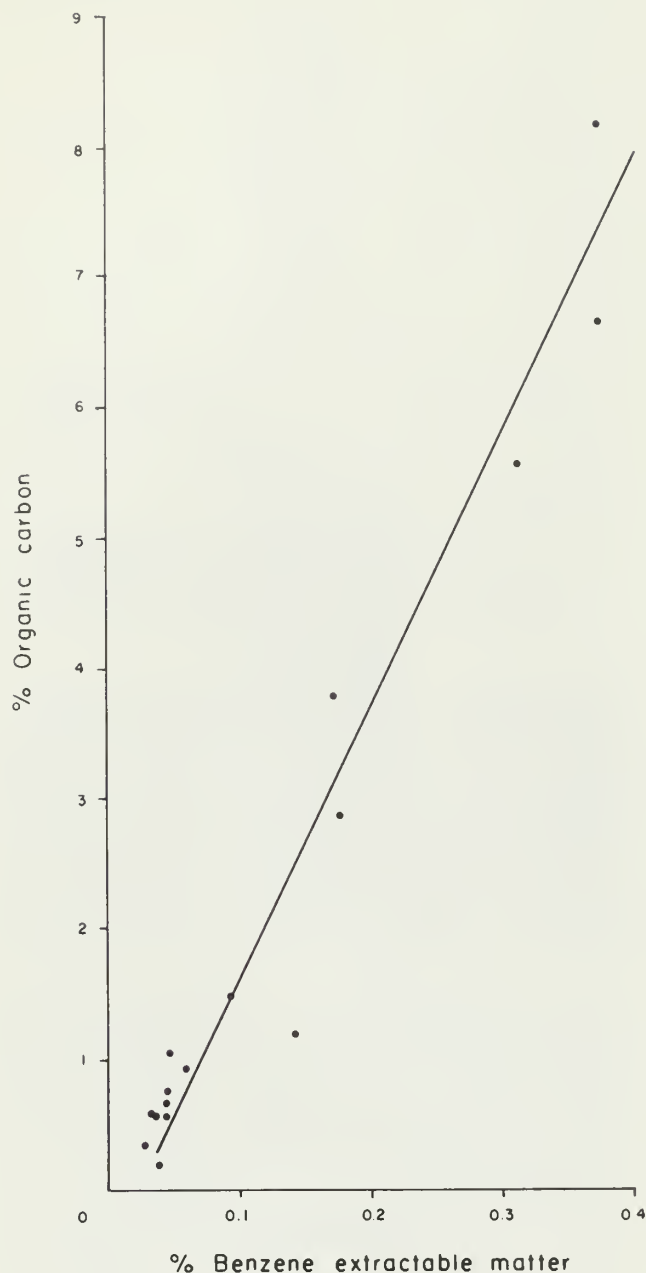
Fig. 4 - Percentage of organic carbon versus percentage of benzene extractable organic matter.

contours are based on about 350 datum points. The organic carbon content ranges from over 9 percent in southwestern Montgomery County to less than 1 percent in several places, principally along the Mississippi River. One small area in southernmost Champaign County also contains less than 1 percent organic carbon.

Figure 5 shows that the location of the oil pools in the Hunton Limestone Megagroup is not related to the variations in organic carbon content of the bottom portion of the New Albany Shale. Some pools are located under areas of high organic carbon (in excess of 7 percent), whereas others coincide with very low organic carbon areas (less than 1 percent). A possible explanation for this is that the New Albany Shale is an adequate source rock of petroleum even in the areas where organic carbon values are lowest. Some Russian geochemists have proposed minimum organic carbon values that must be obtained before a rock can be considered an adequate petroleum source rock. These minimum values range from 2 to as low as 0.5 percent (Timofeev, 1958). The organic carbon content of the New Albany samples studied for this report nearly always exceeded 1 percent and averaged over 4 percent.

Figure 4 shows that the amount of benzene extractable material is present in quantities exceeding 1/20 of the total organic carbon. The amount of extractable material may be a measure of source rock quality. Table 1 shows a classification of source rocks proposed by Philippi (1956, p. 33). This classification is based on indigenous hydrocarbon content of the rock. Assuming that the benzene extractable material used in this study approximates the amount of indigenous hydrocarbons, the same type of classification can be ap-

TABLE 1 — CLASSIFICATION OF PETROLEUM SOURCE ROCKS BASED ON HYDROCARBON CONTENT*

	Indigenous hydrocarbon content	
Source-rock quality	In parts per million of dry sediment	In barrels per acre-foot†
Excellent	>5000	>120
Very good	1500–5000	35–120
Good	500–1500	12–35
Fair	150–500	3.5–12
Poor (marginal commercial)	50–150	1.2–3.5
Very poor (noncommercial)	0–50	0–1.2

*(After Philippi, 1956)

†In the conversion of parts per million into barrels per acre-foot hydrocarbon density is assumed to be 0.9 and the rock density 2.7.
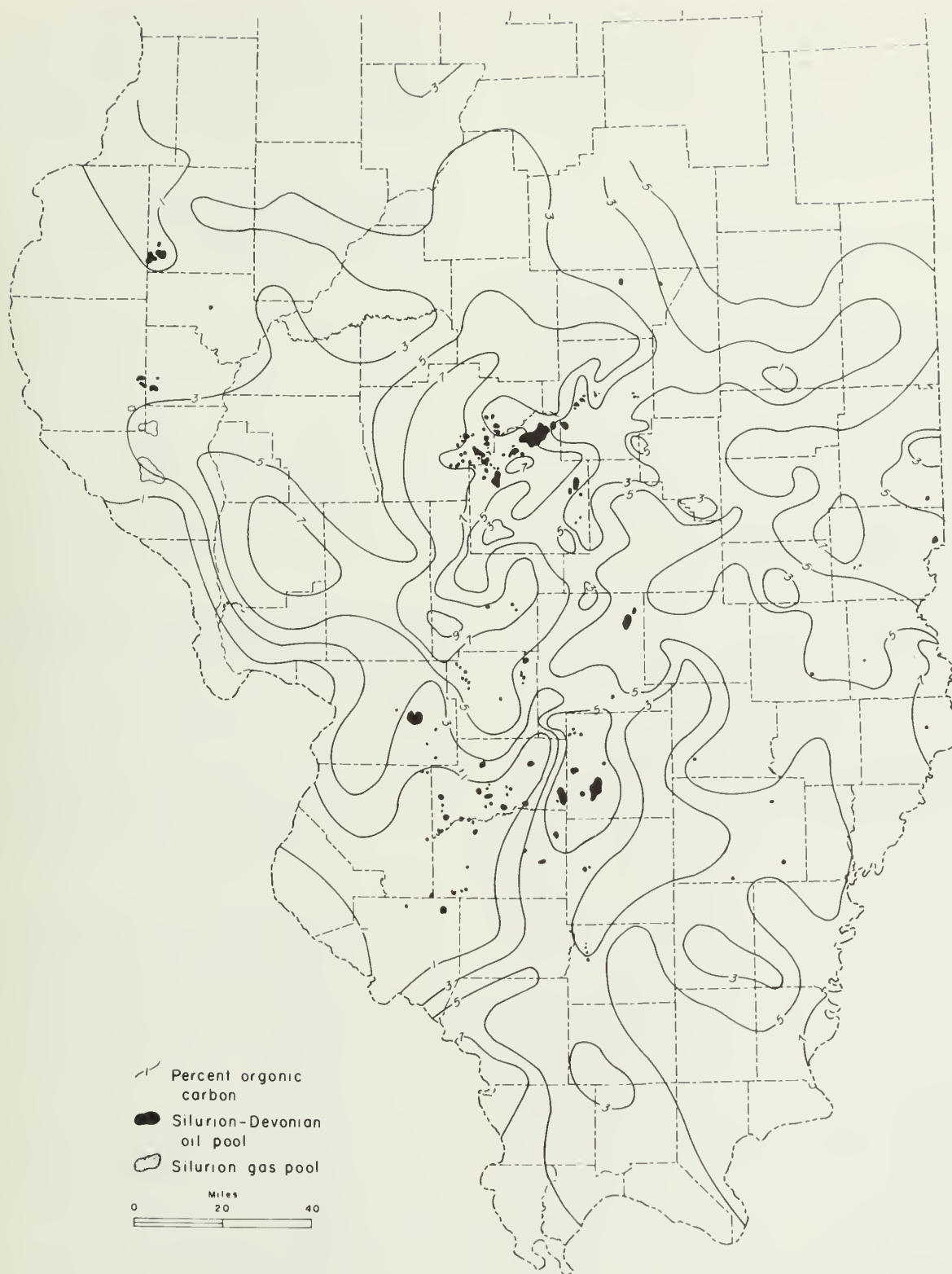
Fig. 5 - Contour map showing organic carbon content of the bottom 50 feet of the New Albany Shale.

plied to the New Albany. Use of this classification to evaluate the source qualities of the shale in the Miller #1 G. W. Sample core (fig. 3) shows almost the entire lower 100 feet to be of very good quality. The only exception is the bottom 7 feet that fell just below the limit for this quality.

COMPARISON OF EXTRACTED MATERIAL TO CRUDE OIL

The composition of the material extracted from the New Albany Shale varied somewhat, but a typical sample is roughly 30 percent aliphatics, 20 percent aromatics, and 50 percent asphaltenes. Several Devonian and Silurian crude oil samples averaged about 50 percent aliphatics, 20 percent aromatics, and 30 percent asphaltenes. The difference in the proportions of the types of compounds is not as important as the fact that the types of compounds found in crude oil are available in the New Albany Shale. Differences in solubilities of the various compounds in water could account for changes in their relative concentrations when migrating from source rock to reservoir. These differences are great enough that attempts to link crude oils to their source rocks by chemical properties have not been particularly successful (Brenneman and Smith, 1958).

There is no way to determine how much hydrocarbon has been removed from the New Albany Shale in the interstitial water that was expelled during compaction of the clay. The present average organic carbon content of the bottom 50 feet of the New Albany is about 4 percent or 1/25 of the total weight of the rock. Of this organic carbon fraction, about 5 percent or 1/20 is in the form of benzene soluble organic compounds. Therefore, these extractable compounds make up about .2 percent of the total weight of the shale.

The total volume of rock sampled is about 355 cubic miles. The organic carbon in this volume of shale amounts to about 15×10^{10} (150 billion) tons, of which 7.2×10^9 (7.2 billion) tons are benzene soluble compounds. This is equivalent to approximately 50 billion barrels of benzene extractable material. The large amount of oil this represents is of no commercial importance because there is no way to extract it economically.

Certainly our laboratory method of extracting organic matter from the shale is much more thorough than any mechanism that occurred in nature where water was used as a solvent rather than benzene. Whatever the process, a very large quantity of organic material, some in the form of hydrocarbon, was available.

The total oil in place contained in all known pools in the Hunton Megagroup is probably about 500 million barrels. This is equivalent to about 1/100 or 1 percent of the benzene soluble oil-like material remaining in the overlying 50 feet of New Albany Shale.

This concentration of extractable organic material is of the same order of magnitude as that found in previous studies. Work done by the Carter Research Laboratory in 1949 revealed that most marine shales that were examined contained extractable organic material in small amounts, ranging from .1 to .5 percent (Hunt and Jamieson, 1958, p. 736). Hunt (1961) calculated a ratio of 1:94 for oil in commercial accumulation in reservoir rocks to the oil in nonreservoir rocks. This closely agrees with the 1:100 ratio obtained by comparing the volume of Silurian-Devonian oil with that of extractable organic material in the bottom 50 feet of the New Albany Shale.

CONCLUSIONS

Although it has not been proven that the New Albany Shale Group supplied the oil found in the Hunton Limestone Megagroup in Illinois, some conclusions can be made:

(1) The volume of hydrocarbon present in the bottom 50 feet of the New Albany Shale is approximately 100 times greater than the total volume of oil in all the known reservoirs in the underlying Devonian and Silurian rocks.

(2) Small amounts of hydrocarbons were probably present in the organic material deposited with the New Albany Shale. These hydrocarbons then increased in volume with time and depth of burial as a result of thermal, nonbiological processes.

(3) As the clays of the New Albany were compacted, the water that was expelled from them probably carried with it small amounts of hydrocarbon in solution or colloidal dispersion.

(4) Some of this expelled water would have traveled downward into porous parts of the underlying Devonian and Silurian carbonates.

The only requirements needed to form a commercial oil pool are conditions that cause the precipitation or filtering of this oil from the water and the trapping of it in sufficiently large volumes. These conditions are necessary regardless of where the oil was generated.

Many questions concerning petroleum source rocks are yet to be answered, but in the case of the oil in the Hunton Limestone Megagroup in Illinois, the New Albany Shale appears to be the most likely source.

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